PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

IPR FORMALITIES

P 1327/WO

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RECEIVED

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Rule 71.1)

Date of mailing *(day/month/year)*	23.12.2004
Applicant's or agent's file reference: P1327/WOD	**IMPORTANT NOTIFICATION**

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/GB 03/03440	06.08.2003	22.08.2002

Applicant: THE SECRETARY OF STATE FOR DEFENCE et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.

2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.

3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. **REMINDER**

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

The applicant's attention is drawn to Article 33(5), which provides that the criteria of novelty, inventive step and industrial applicability described in Article 33(2) to (4) merely serve the purposes of international preliminary examination and that "any Contracting State may apply additional or different criteria for the purposes of deciding whether, in that State, the claimed inventions is patentable or not" (see also Article 27(5)). Such additional criteria may relate, for example, to exemptions from patentability, requirements for enabling disclosure, clarity and support for the claims.

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PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference P1327/WOD	**FOR FURTHER ACTION**	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/GB 03/03440	International filing date *(day/month/year)* 06.08.2003	Priority date *(day/month/year)* 22.08.2002
International Patent Classification (IPC) or both national classification and IPC G01N21/71		
Applicant THE SECRETARY OF STATE FOR DEFENCE et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 9 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 23 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the opinion
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☐ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
25.02.2004	23.12.2004
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer Duijs, E Telephone No. +49 89 2399-7945

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB 03/03440

I. Basis of the report

1. With regard to the **elements** of the international application *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*:

Description, Pages

1-5	as originally filed
6-25	received on 24.08.2004 with letter of 18.08.2004

Claims, Numbers

1-14	received on 24.08.2004 with letter of 18.08.2004

Drawings, Sheets

1/1	filed with the demand

2. With regard to the **language,** all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

   These elements were available or furnished to this Authority in the following language: , which is:

   ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).

   ☐ the language of publication of the international application (under Rule 48.3(b)).

   ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

   ☐ contained in the international application in written form.

   ☐ filed together with the international application in computer readable form.

   ☐ furnished subsequently to this Authority in written form.

   ☐ furnished subsequently to this Authority in computer readable form.

   ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

   ☐ the description, pages:

   ☐ the claims, Nos.:

   ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

   (Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-12
	No:	Claims	13,14
Inventive step (IS)	Yes:	Claims	1-12
	No:	Claims	13,14
Industrial applicability (IA)	Yes:	Claims	1-14
	No:	Claims	

2. Citations and explanations

   see separate sheet

Re Item(s) V(-VIII)
Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Reference is made to the following documents:

D1: US-A-5443793	D2: US-A-5241179
D3: US-A-4247770	D4: GB-A-2169496
D5: US-A-5847825	D6: US-A-6008897

2. Novelty (Art. 33(2) PCT):

The subject-matter of **apparatus claims 13 and 14** does not meet the criteria of Article 33(2) PCT with respect to novelty for the following reasons:

2.1 Independent apparatus **claim 14**:

Document **D2** discloses (the references in brackets refer to D2):
-- An apparatus *suitable for* (see the PCT Guidelines S-07/1998, III-4.8) stand off analysis of a sample comprising one or more chemical and/or biological warfare agents of low volatility (abstract, first line; col. 1, lines 15-32; fig. 1);
-- (i) an excitation means 11 (col. 2, lines 33-36; col. 4, lines 35-40) *arranged such that it can be used to* (interpreted as "suitable for", PCT Guidelines S-07/1998, III-4.8) vaporise the sample thereby producing a vapour plume of molecular species (col. 7, lines 20-35);
-- (ii) an analytical means (col. 2, lines 28-33; col. 5, line 38 - col. 6, line 4) *arranged to* (interpreted as "suitable for", PCT Guidelines S-07/1998, III-4.8) analyse the emission spectra of the molecular species within the vapour plume (col. 5, lines 31-33; although emissive light rays from the surface, transmitted through the vapour cloud, are detected and analysed as absorption bands, the analytical means is also suitable for detecting/analysing direct emission of the molecular species within the vapour plume);
-- (iii) means 19, 21, 29 (fig. 1; col. 5, lines 1-4, 31-39) associated with the analytical means *to enable* said analytical means to receive the emission spectra from the vapour plume.

2.2 What has been said above with reference to apparatus claim 14 ("apparatus")

concerns **apparatus claim 13** ("kit") mutatis mutandis.
Although 13 and 14 have been drafted as separate independent claims, they relate to exactly the same subject-matter and differ from each other only in respect of the terminology used (kit/apparatus). The aforementioned claims therefore **lack conciseness** (see comments in paragraph 5 below).

2.3 Hence, **independent claims 13 and 14** are not novel (Art. 33(2) PCT).

3. Inventive Step (Art. 33(3) PCT):

The comments on clarity (Art. 6 PCT) in paragraph 5 below have to be taken into account.

The subject-matter of **method claims 1-12** meets the criteria of Article 33(2) and 33(3) PCT with respect to novelty inventive step for the following reasons:

3.1 Independent method **claim 1**:
The documents D1 and D2 are both regarded as being the closest prior art to the subject-matter of claim 1:

3.1a The document **D1** discloses (the references in parentheses applying to this document):
-- A method, suitable for stand off analysis of a sample comprising one or more chemical and/or biological warfare agents (fig. 1; col. 1, lines 11-13, 42-51);
-- (i) using an excitation means 12 to *excite* the sample vapour plume of molecular species (col. 2, lines 32-46);
-- (ii) using an analytical means 15, 16, 18 (photo-detector, notch filter, controller; "to analyse" = "to identify and measure the chemical constituents of a substance or specimen"; a photo detector combined with a filter is able to analyse a sample) to analyse the molecular species within the vapour plume, wherein the analytical means 15, 16, 18 analyses the molecular emission spectra of the vapour plume and is provided with *means* 15 to enable it to receive said spectra for stand off analysis (see fig. 1; col. 1, lines 42-51; col. 2, lines 49-65).

Problem: D1 discloses the remote detection of harmful gases or fumes comprising pollutants, such as warfare agents. The emission of the molecules in said gases is detected and analysed. However, in the battle field the pollutants are

not always present in the gaseous form. The **technical problem** to be solved by the present invention may therefore be regarded as "how to adapt the method for detecting other or non-gaseous samples".

Solution: The subject-matter of claim 1 differs from D1 in that (a) said sample comprises agents **of low volatility**, and in that (b) said excitation means is used **to vaporise** the sample **thereby producing** a vapour plume of molecular species.

Although, at a first glance, this solution seems to be obvious for a man skilled in the art knowing the disclosure of D1, no hint for this solution can be found in the prior art documents:
- D1 only discloses the measurement of gasses and fumes. The document is silent about "low volatile", liquid or solid samples which would have to be vaporised;
- Although **D2** discloses the remote detection of low-volatile contaminants, output spectra are generated by the liquid sample directly rather than by a vaporised portion thereof (see col. 7, lines 45-49);
- Although in **D3-D6**, a sample is vaporised and remotely analysed, no vapour plume of molecular species is generated. The emission of a plasma, atoms, or ions is detected and analysed.

3.1b The document **D2** discloses (the references in parentheses applying to this document):
-- A method, *suitable for* (see the PCT Guidelines S-07/1998, III-4.8) stand off analysis of a sample comprising one or more chemical and/or biological warfare agents of low volatility (abstract, first line; col. 1, lines 15-32; fig. 1);
-- (i) using an excitation means 11 (col. 2, lines 33-36; col. 4, lines 35-40) to vaporise the sample thereby producing a vapour plume of molecular species (col. 7, lines 20-35);
-- (ii) using an analytical means (col. 2, lines 28-33; col. 5, line 38 - col. 6, line 4) to analyse the molecular species within the vapour plume, wherein the analytical means analyses emission spectra (col. 5, lines 31-33; emissive light rays from the surface, transmitted through the vapour cloud, are detected and analysed as absorption bands) and
-- is provided with means 19, 21, 29 (fig. 1; col. 5, lines 1-4, 31-39) to enable it to receive said spectra for stand off analysis.

Problem: The analytical process which is the basis of D2 is quite distinct from

what is used in the present invention. In D2 the background or surface is heated and emissive light rays from the surface, transmitted through the vapour cloud of volatile sample, are detected and analysed as absorption bands. Although D2, additionally to volatile samples, also discloses the remote detection of low-volatile contaminants, output spectra are generated by the liquid sample directly rather than by a vaporised portion thereof (see col. 7, lines 45-49). The **technical problem** to be solved by the present invention may therefore be regarded as "to provide an alternative method for detecting low-volatile samples".

Solution: The subject-matter of claim 1 differs from D2 in that in case that said sample comprises agents of low volatility, (a) a vapour cloud of said low-volatile sample, and (b) the analytical means analyses the molecular emission spectra of the vapour plume.

No hint for this solution can be found in the prior art documents (see the comments given for D1 and D3-D6, above).

3.1c Hence, **claim 1** can be regarded as being novel (Art. 33(2) PCT) and inventive (Art. 33(3) PCT).

3.2 **Claims 2-12** are dependent on claim 1 and as such also meet the requirements of the PCT with respect to novelty and inventive step.

4. Industrial applicability (Article 33(4) PCT):

The requirement of Art. 33(4) PCT as to industrial applicability is fulfilled for all claims.

5. Further comments, e.g. on clarity (for the sake of completeness):

5.1 Although **apparatus claim 13 (kit) and apparatus claim 14 (apparatus)** have been drafted as separate independent claims, they **relate to exactly the same subject-matter** and differ from each other only in respect of the terminology used (kit/apparatus). The aforementioned claims therefore **lack conciseness.**

It appears that by filing separate independent claims for a "kit" and an

"apparatus", it was intended to cover different entities, i.e. firstly, where the equipment is presented as a single unitary item (apparatus), or secondly, where the elements of the equipment are independent and form an equipment only once assembled together (kit).

However, **claims relating to a "kit" and to an "apparatus" relate both to the same "physical entity"** (see the PCT Guidelines S-07/1998, III-3.1):
- The apparatus comprises all the technical features or elements of the kit assembled together;
- Protection of the kit, with its elements **assembled together**, or of the **apparatus as a whole**, comprising all the technical elements or features of the kit assembled together, is covered by the wording of the apparatus claim;
- **The separate elements of the kit are not protected** by the wording of the apparatus claim. In such a case one or more separate independent claim(s) for one or more separate element(s) should have been filed, thereby taking into account Rule 13 PCT (unity);
- The apparatus claim is **not** limited to "unitary item", whereby all the technical features of said item are **not** suitable for being separated, e.g. for transport. The wording of the apparatus claim also covers an assembly of elements which can be separated.

Therefore, a separate independent claim for a "kit" is superfluous and inconcise, and **apparatus claims 13 and 14** do not meet the requirements of Article 6 PCT.

5.2 The **relative term "low** volatility" used in **claims 1, 13, and 14** has no well-recognised meaning and leaves the reader in doubt as to the meaning of the technical feature to which it refers, thereby rendering the definition of the subject-matter of said claims unclear, Article 6 PCT (see also the PCT Guidelines S-07/1998, III-4.5). In the description on page 10, lines 15-16, a clear alternative for the term "low volatility" is mentioned.

5.3 The **vague and imprecise statement** "without departing from its **spirit** or scope" on page 24, lines 4-5" implies that the subject-matter for which protection is sought may be different to that defined by the claims, thereby resulting in lack of clarity (Article 6 PCT) when used to interpret them (see also the PCT Guidelines, III- 4.3a).

5.4 The **unit "atm"** employed on page 11, last four lines is not recognized in

international practice (not a SI unit), contrary to the requirements of Rule 10.1(d) PCT. The unit "Pa" or "bar" should be used instead.

5.5 The **relative term "about"** used in **claims 4, 5, and 10,** which is vague and imprecise and leaves the reader in doubt as to the meaning of the technical feature to which it refers, thereby rendering the definition of the subject-matter of said claims unclear (Article 6 PCT), has been removed from said claims. However, **the description** (see for example page 18, first paragraph; page 19, second paragraph) **has not been amended accordingly** to the amendments carried out in the claims. Said claims are, therefore, not fully **supported** by the description.

5.6 Claim 1 is not in the **two-part form** as defined in Rule 6.3(b) PCT.

the substrate to the contaminant, heating the substrate sufficiently may require an unduly large amount of energy, and that the contaminant may produce both absorption and emission spectra which lead to a false negative result.

There remains a need to develop an improved method, and associated apparatus, that enables quick and accurate stand-off analysis and positive quasi real time in the field identification of solids and liquids, particularly those with low volatility. In order to be able to be used in a stand-off manner it is important that the method does not operate at wavelengths that would be masked by the absorption bands of the atmosphere itself. The method should be flexible enough to be used with a wide variety of different materials, should be able to identify individual compounds when presented with a mixture of compounds, and should have sufficient selectivity to be able to differentiate between closely related compounds. Such a method should be sensitive enough to be useable even when only a very small amount of the material is present or the material is present at a low concentration. The problem also remains as to how to achieve this technical result with equipment which is easy to transport to the front line during a military campaign, can be operated by personnel with little or no specific scientific training, can be used to equal effect in a wide variety of different in-field situations, including for identification of land or water contamination, and does not require the arrangement of complex optical or filtering means around the sample, or access to the sample from specific angles, for effective operation.

A method and associated apparatus has now been developed which allows for stand-off interrogation and accurate analysis of a wide range of materials including solids and liquids with low volatility. The method comprises a first step in which an

excitation means, preferably a laser operating at a single wavelength which is not necessarily related to the absorption characteristics of the sample, is used to volatilise the sample to produce a vapour plume of molecular species which are excited. In a second step a stand-off analytical means, for example an infrared spectrometer preferably fitted with a means for collecting light from the sample, is used to analyse the molecular emission spectra of the vapour plume. In order to achieve the desired level of analytical selectivity this method has been designed to analyse the molecular spectral characteristics, including vibrational characteristics, of the sample. This method has also been designed such that the analytical step does not rely on the use of a second energy source to further excite the sample to create secondary emission or fluorescence thereby reducing the complexity of the method. This method and associated apparatus have several advantages over the prior art including that they provide an accurate means for remotely interrogating and analysing a wide variety of materials including solids and liquids with low volatility across a broad wavelength spectrum, and which relies only on a single excitation means and whereby the excitation means can be a single wavelength non-specific laser. The method is sensitive enough to be used when only low levels of the sample are present, can identify components when presented with a mixture of materials, and is also sufficiently selective to differentiate between closely related materials in real time or quasi real time. Furthermore the method is flexible such that there is no special need for the laser and the analytical instrument to have a specific orientation with respect to either each other or the sample, nor is there a requirement for the use of additional lenses or filters to achieve the spectroscopic effect. This means that the instrumentation associated with the method can be designed to be small and portable for use at the front line and can be used even when it is not possible to have access to

the sample from all possible angles. Finally the instrumentation is relatively simple ensuring that it can be readily used by personnel with little or no specific scientific training.

It is an object of the present invention to develop a method and associated apparatus capable of stand-off interrogation and analysis of a wide variety of materials including liquids and solids with low volatility. It is another object of this invention to develop such a method to be sensitive enough to be useable when only low level of samples are present, to have the capability to identify components of a mixture, and is selective enough to differentiate between closely related materials. It is a further object of this invention to develop such a method that is able to provide real time or quasi real time analysis. It is also an object of this invention to develop an apparatus that is portable so that it can be readily used in a variety of different situations, including at the front line during a campaign, and that it can be readily operated by non-scientifically trained personnel. These, and other objects of this invention, will become apparent in light of the following disclosure.

Summary of the Invention

According to a first aspect this invention relates to a method, suitable for stand off analysis of a sample (2) comprising one or more chemical and/or biological warfare agents of low volatility, said method comprising:

(i) using an excitation means (6) to vaporise the sample thereby producing a vapour plume (10) of molecular species; and

(ii) using an analytical means (12, 18) to analyse the molecular species within the vapour plume wherein the analytical means analyses the molecular emission spectra of the vapour plume and is provided with means (14) to enable it to receive said spectra for stand off analysis.

According to a second aspect, this invention relates to a kit suitable for stand off analysis of a sample (2) comprising one or more chemical and/or biological warfare agents of low volatility, said kit comprising:

(i) an excitation means (6) arranged such that it can be used to vaporise the sample thereby producing a vapour plume (10) of molecular species;

(ii) an analytical means (12, 18) arranged to analyse the emission spectra of the molecular species within the vapour plume; and

(iii) means (14) associated with the analytical means (12, 18) to enable said analytical means to receive the emission spectra from the vapour plume.

According to a third aspect, this invention relates to an apparatus suitable for stand off analysis of a sample comprising one or more chemical and/or biological warfare agents of low volatility, said apparatus comprising:

(i) an excitation means (6) arranged such that it can be used to vaporise the sample thereby producing a vapour plume (10) of molecular species;

(ii) an analytical means (12, 18) arranged to analyse the emission spectra of the molecular species within the vapour plume; and

(iii) means (14) associated with the analytical means (12, 18) to enable said analytical means to receive the emission spectra from the vapour plume.

Detailed Description of the Invention

The elements of the apparatus are described in more detail below.

As used herein the term "remote" shall be taken to mean that an operator of an instrument is not co-located with a sample but that some feature of the instrumentation is co-located with the sample.

As used herein the term "stand-off" shall be taken to mean that neither an operator nor any element of instrumentation is co-located with a sample. As such when an apparatus is stand-off there is no risk of sample contamination to either personnel or equipment.

As used herein the term "vaporise" shall be taken to mean that at least some of the sample has been converted to a vapour.

As used herein the term "low volatility" shall be taken to mean that, at atmospheric temperature and pressure, the sample has a vapour pressure less than that of water.

As used herein the term "molecular species" shall be taken to mean a species that comprises one or more atoms linked by chemical bonds and whereby at least one of these bonds is consistent with at least one of the bonds present in the parent sample. The molecular species may be neutral or charged.

As used herein the term "plume" shall be taken to mean a cloud of vapour. There will be many different types of molecular species that will be present in the plume and

these will likely comprise a mixture of one or more of the vaporised parent sample materials, fragment species obtained by dissociation of one or more of the chemical bonds in the parent sample, or ionised species of the parent material or fragments.

The present invention relates to a method, suitable for stand off analysis of a sample (2) comprising one or more chemical and/or biological warfare agents of low volatility, said method comprising:

(i) using an excitation means (6) to vaporise the sample thereby producing a vapour plume (10) of molecular species; and

(ii) using an analytical means (12, 18) to analyse the molecular species within the vapour plume wherein the analytical means analyses the molecular emission spectra of the vapour plume and is provided with means (14) to enable it to receive said spectra for stand off analysis.

The method is a stand-off method enabling the positive identification of a sample material. It has been designed to be flexible such that it can be used in a wide variety of different locations. The sample is contained on a substrate within a target area. Suitable substrates include land and water, preferably land. Examples of land substrates include sand, concrete, tarmac, asphalt, soil, grass and the like. Since the method relies on the production of a vapour plume from the sample material it cannot in general be used in an environment where there is not a gaseous atmosphere for example underwater, but with the exception that it could be conducted in a vacuum or partial vacuum if required.

The method of the present invention has been designed such that it can be used for a wide variety of chemical and biological warfare agent samples that have a low

volatility at atmospheric temperature and pressure. The sample to be analysed is optionally a solid or a liquid, preferably a liquid and more preferably an organic liquid. It is preferred that, at 20°C and 1Atm pressure, the sample has a vapour pressure of less than about 0.02Atm, preferably less than about 0.001Atm, and more preferably less than about 0.0001Atm. Furthermore the method has been designed such that, if a sample comprises more than one different component, it can positively identify individual components. As such the sample to be analysed may comprise a mixture of one or more of a solid material, a mixture of one or more of a liquid material or a mixture of one or more of a solid material in conjunction with one or more of a liquid material. The sample may optionally comprise one or more carrier materials or thickening agents. In addition the sample may be a solution, suspension, or a colloid or other type of mixture. Furthermore the method has been designed such that it is selective enough to be able to positively differentiate between different components within a sample including to identify carrier components, and it may also differentiate between different components which are closely related or of a similar nature.

In order that the method is able to work effectively it must be possible to vaporise at least a small amount of the sample from the surface of the substrate. As such the sample to be vaporised should preferably be present on the surface of the substrate but the method may also be used if the material has been absorbed only a short distance into the substrate or if the sample is present in solution within the substrate. In order to allow for such circumstances, the method of the present invention is sensitive enough that it can be usefully used to analyse material when even only a very low level of pollutant is present. For example the method of the present invention is able

to positively identify a material when presented with as little as a droplet or grain with a diameter of as small as 0.1mm, or more likely as small as 1mm. There is no maximum restriction on the size of the contaminant that can be successfully analysed with this method. In addition, when the sample is a solution or mixture of one or more materials in a solvent or other carrier material, the method is sensitive to be able to identify the relevant components when the material is present at only very low concentrations, for example if the material is present at a concentration of about 1mM, or even 1μM.

The method of the present invention uses an excitation means to vaporise the sample. In order for the method of the present invention to have sufficient sensitivity and selectivity it is necessary that the excitation means only uses sufficient excitation power to vaporise the sample to produce a vapour plume wherein at least some of the molecular integrity of the sample itself has been maintained. As such the vapour plume should comprise at least one molecular species comprising at least one of the chemical bonds present in at least one of the components of the parent sample. The excitation step may interact with the one or more components of the sample material to cause dissociation or ionisation. However, in order to obtain good spectral data, it is essential that, for each component present in the sample, the plume comprises at least some of the component in a non-dissociated and non-ionised state, ie. in the form of molecular species. In addition it is preferred that the excitation means does not result in the ionisation of the atmosphere or the substrate and it is necessary that the excitation step does not result in the formation of a plasma. As such, samples which have an extremely low volatility, for example metals, are unlikely to be readily analysed using this method since it would be very difficult to identify an excitation

means which is able to produce a vapour plume from the sample without dissociating the sample completely and / or producing a plasma. The excitation means should excite the molecular species within the vapour plume sufficiently so that the vapour plume is hotter than the surrounding atmosphere by at least about 0.1K, preferably by about 1K, and more preferably by about 5K. When the vapour plume is sufficiently excited it is described as a hot vapour plume.

Once sufficient sample has been volatilised then the excitation means can be turned off which saves power. This method does not require that the background is heated, or that a bulk sample is heated, or that a plasma is produced. This further reduces the level of energy required from the excitation means making the method ideal for use in the field where power requirements may be at a premium. The actual level of energy required by the excitation means will vary depending on several factors including the likely nature of the contaminant, the nature of the excitation means, the distance of the excitation means from the sample and also the atmosphere in which the method will be operated. The level of energy for any particular scenario can be readily determined by one skilled in the art.

In the method of the present invention the excitation means is directed towards the sample material on a suitable substrate. In the field this will usually be the ground or water. Provided that sufficient energy from the excitation means reaches the sample to enable it to be vaporised, then there is no requirement that the excitation means be able to be accurately focussed on the sample. This has the advantage that the excitation means can be used to vaporise a sample from a long distance or in the instance where the exact location of even a low level of contaminant may not be

precisely known. However, the more accurately the excitation means can be focussed on the sample within the target area, the less the power that will be required to vaporise the sample. As such it is preferred that the excitation means can be accurately focussed such that it can be targeted directly to the sample where possible. To enable the excitation means to be more accurately directed towards a sample on a substrate, it is possible to raise the excitation means onto a platform. The height of such a platform may vary considerably from instance to instance but can be determined by one skilled in the art determining the distance of the sample, the focal length of the excitation means, the angle to the sample, the curvature of the earth and the like. However for practical reasons it is preferred that the height of the platform is not higher than about 10m, preferably not higher than about 5m.

In order that the method of the present invention is able to usefully be used in a stand off mode for the analysis of a sample it is preferred that the excitation means can effectively vaporise at least some of the sample at a distance of greater than about 10m, preferably greater than about 30m, more preferably greater than about 50m and most preferably greater than about 100m from the sample. At such distances it may be necessary to raise the excitation means to a height of from about 1m to about 20m, preferably less than about 10m, more preferably less than about 5m and most preferably about 3m above the substrate to be able to direct the excitation means towards the sample as accurately as possible. The exact height required will depend on the distance of the sample and the focussing angle from the instrument to the sample. Any suitable means can be used to raise the means for example a tower or platform. However, since it is envisaged that this equipment would be used in the field by ground forces or personnel, it is unlikely that the range of the excitation

means would be required to be greater than 1000m. When used at long distances it may be necessary for one skilled in the art to adjust the excitation means accordingly to achieve the desired sample vaporisation. In performing such an adjustment it is necessary to consider whether or not the wavelength of the excitation means is on or off resonance with an absorption band of the sample itself, the manner in which the energy is delivered and the required focussing of the excitation means. By adjusting each of these with respect to each other, an excitation means can be achieved whereby the sample is heated most efficiently to produce a vapour plume.

The preferred excitation means for use with the method of the present invention is a laser because the power of the laser can be controlled and the laser beam can be focussed to target a specific area. This latter feature means that lasers are ideally suited for use when only a low level of sample is present and means that the instrument can be used flexibly in instances where the sample is at different distances from the user. Lasers for use with the present invention can operate at any wavelength provided they can deliver sufficient power to vaporise at least some of the sample. They can be operated as tuneable wavelength lasers or fixed wavelength lasers. In order for this method to operate effectively there is no requirement that the laser beam be tuneable to any specific wavelength related to the absorption bands of the sample in question. Thus, in order to reduce complexity and minimise costs, it is preferred that the laser is operated at a fixed wavelength. Since the method does not rely on collecting data at a specific wavelength, the chosen fixed wavelength of the laser need not necessarily be related to any given absorption wavelength of any species in the sample. Again provided that the laser delivers sufficient power, the laser can be operated as a pulsed laser or as a continuous wave laser. It is preferred

that the laser is a continuous wave laser since this is more likely to provide a continuous stream of vapour for analysis. It is further possible that if the laser is a continuous wave laser that it be a modulated continuous wave laser. This is preferred since it can be used in combination with appropriate detection means capable of demodulating or otherwise processing the signal to achieve a higher level of detection sensitivity and can also result in the avoidance of non modulated signals which may otherwise interfere with the results.

Suitable powers for a continuous wave laser are greater than about 2 watts, more preferably greater than about 5 watts, and even more preferably greater than about 10 watts or equivalent. However it is important that the power of the laser is not so large as to, within the plume, dissociate all of the molecular species to form atoms or ions as a plasma or otherwise. This is because such plasma would be of insufficient selectivity for use in the present invention. As such it is preferred that a continuous wave laser has a power of less than about 150watts, more preferably less than about 50watts and even more preferably less than about 20 watts. If the excitation means is a laser, but is not a continuous wave laser, for example if it is a pulsed laser, then a power equivalence to the above should be used and these can be determined readily by one skilled in the art according to the system in question. For a pulsed laser the power level should be selected such that mean power delivered to the sample is equivalent to that of a continuous wave laser.

A wide variety of different lasers can be used in the method of the present invention including Neodymium Yttrium Aluminium Garnet laser; Titanium sapphire laser; carbon dioxide laser. The preferred laser type is a carbon dioxide laser. Alternatively

the laser could optionally be based around an optical parametric oscillator, such as those known in the art, specifically configured to provide tuneable infrared radiation.

The method of the present invention uses an analytical means to analyse the molecular species within the vapour plume wherein the analytical means is capable of analysing the molecular emission spectra of the vapour plume. Any suitable analytical means may be used. To minimise the complexity of the equipment it is preferred that the analytical means is able to analyse the vapour plume without an additional need for secondary excitation of the vapour plume. Furthermore it is also preferred that, in order to obtain the necessary analytical signals from the sample, there is no requirement for the background to be excited to provide a radiation emission source. One advantage of this simplicity is that the method of the present invention need only comprise the use of a single excitation means. Utilising an analytical means that is capable of analysing the molecular emission spectra of the vapour plume is one means by which the secondary excitation of the sample may be avoided.

One example of a suitable technique is infrared spectroscopy. In order to be able to use infrared spectroscopy to analyse the emission spectra of the molecular species in the vapour plume it is necessary that the temperature of the vapour plume is hotter than the surrounding atmosphere by at least about 0.1K, preferably by about 1K, and more preferably by about 5K. A further advantage of infrared spectroscopy is that it is a technique with the inherent sensitivity and selectivity properties that make it ideal for allowing for the accurate identification of, and differentiation between, a wide variety of different materials and also it can be used in atmospheric conditions

without fear of any emission spectra from the background interfering with the spectral data of the sample in question. In addition, by comparing the results with known libraries of data it is possible for infrared spectroscopy to be used to identify individual components in a mixture of materials. In accordance with above, it is preferred that the analytical means is an infrared spectrometer. In order to enhance the analytical capability of the infrared spectrometer it is preferred that the spectrometer is a rapid scanning infrared spectrometer and more preferably a rapid scanning Fourier transform infrared spectrometer or other measurement and processing technique for example image multi-spectra sensing as disclosed in US 5,479,258.

It is preferred that the analytical means is linked to a computer which is able to employ software to process the analytical data and provide a meaningful result for the user. The computer preferably has a memory having a library of analytical data that have been developed under controlled conditions for likely known contaminants at known concentrations. The computer compares the data obtained to the known data in its library. It is preferred that either a peak identification technique or other quantitative data analysis technique is employed. By this analysis the identity of the contaminant material in the target area can be determined. The computer preferably operates continuously such that the analysis of the vapour sample can proceed simultaneously or nearly simultaneously thereby providing real-time or near real-time monitoring.

In order that the method of the present invention may be used in a stand-off manner the analytical means is fitted with a means for stand-off detection of the analytical

signals from the vapour plume. One important feature that leads to the success of this method is the ability to analyse the sample material in a stand-off manner without there being any necessity that the sample and the analytical instrumentation are co-located. Example of such means may include one or more of an emission port, one or more lenses or a reflective telescope. It is preferred that the means for the stand-off detection of analytical signals from the vapour plume is an reflective telescope. Examples of reflective telescopes include a Newtonian telescope or a Cassegrain telescope. It is preferred to use a Cassegrain telescope. In order to simplify the operation of the equipment and reduce the risk to personnel it is preferred that the means for stand-off detection of the analytical signals from the vapour plume is able to operate effectively over a distance similar to that over which the excitation means is able to vaporise the sample. If a reflective telescope is being used it is preferred that the field of view of the telescope can be varied such that the instrument can be used flexibly when the sample is at different distances. It is preferred to use an infinity focussed reflective telescope.

Examples of infrared spectrometers which have been fitted with a means for stand-off detection of the analytical signals include OPAG 22 supplied by Bruker Optik GmbH (Rudolf-Plank-Str. 23, 76275 Ettlingen, Germany); MIDAC AM supplied by MIDAC Corporation (17911 Fitch Avenue, Irvine, California, USA); MR Series IR Spectrometers supplied by AB Bomem Inc (585 Charest Boulevard East, suite 300, Quebec, Canada); and the Model 500 Fourier Transform Infrared spectrometer supplied by Block Engineering (72 Cedar Hill Street, Marlborough, Massachusetts, USA).

In order that the analytical means is able to operate effectively it is important to produce sufficient vapour plume that the means for stand-off detection of the analytical signals is able to identify the sample. This requirement will vary considerably from instrument to instrument and will need to be identified by one skilled in the art on a case by case basis. The excitation means will need to be adjusted to ensure that sufficient vapour is produced. In some instruments it may be possible to adjust the field of view of the detection means such that the plume adequately fills the field of view. Optionally the instrument may be fitted with a sight to help to ensure that it is aligned correctly. Optionally the instrument may be fitted with a filter to remove any scattered or reflected laser radiation from the field of view of the analytical means such that the spectral results are not distorted. It is preferred that sufficient vapour plume is produced to at least partially, and preferably fully, fill the field of view of the analytical means. As with the excitation means, it may be helpful to place the analytical means onto a platform in order to enable it to be better directed towards the vapour plume. Here the height of the platform required will be dependent on the distance of the sample, the height of the hot vapour plume above the surface and the angle of the instrument to view the hot vapour plume.

In order to operate the method of the present invention the excitation means must be orientated such that it can be used to vaporise the sample to produce a vapour plume. Similarly the analytical means must be orientated such that the means for stand-off detection of the analytical signals is able to detect the vapour plume. Beyond this there is no specific requirement regarding the relative orientation of the laser with the analytical instrument. The two means should be orientated such that the operation of one does not interfere with the operation of the other. Preferably the means can be

located side by side. Even more preferably the means are integrated into a single apparatus which is capable of performing both the first and second step of the present invention. The method of the present invention may optionally comprise further suitable optics that can be used, if necessary, to enable the accurate focusing of the excitation means onto the sample or to deflect the emitted radiation to the analytical means. It is preferred however that the method does not require such a means since this adds complexity to the system but, in the instance where it is not possible for logistical reasons to co-locate the excitation means with the analytical means, it may provide a useful manner by which to aid alignment of the different means required.

This invention also relates to a kit suitable for stand off analysis of a sample comprising one or more chemical and/or biological warfare agents of low volatility, said kit comprising:

(i) an excitation means (6) arranged such that it can be used to vaporise the sample thereby producing a vapour plume (10) of molecular species;

(ii) an analytical means (12, 18) arranged to analyse the emission spectra of the molecular species within the vapour plume; and

(iii) means (14) associated with the analytical means (12, 18) to enable said analytical means to receive the emission spectra from the vapour plume.

Furthermore, this invention relates to an apparatus suitable for stand off analysis of a sample comprising one or more chemical and/or biological warfare agents of low volatility, said apparatus comprising:

(i) an excitation means (6) arranged such that it can be used to vaporise the sample thereby producing a vapour plume (10) of molecular species;

(ii) an analytical means (12, 18) arranged to analyse the emission spectra of the molecular species within the vapour plume; and

(iii) means (14) associated with the analytical means (12, 18) to enable said analytical means to receive the emission spectra from the vapour plume.

In designing a kit or apparatus for use with the method of the present invention, and for use in the field, it is important to bear in mind the following: making the apparatus as simple to use as possible such that it can be operated by personnel with little or no scientific training; minimising the size and weight of the equipment such that it can be easily transported; maximising the durability of the equipment for different situations, including different temperatures, and minimising the power requirement of the apparatus.

Figures

This invention will now be described by reference to the following drawings in which Figure 1 shows operation of a method according to the present invention.

Figure 1 shows several small droplets of liquid sample 2 resting on the surface of the ground 4. A laser excitation means 6 is situated on the ground 4 approximately 10m away from the liquid sample 2. A radiation beam 8 is emitted from the laser 6 and

focussed on the liquid sample 2. This vaporises the sample 2 to produce a vapour plume 10 directly above the liquid sample 2. An infrared spectrometer analytical means 12 is located alongside the laser excitation means 6 also approximately 10m away from the liquid sample 2. The infrared spectrometer 12 is fitted with a telescope lens 14 that is focussed at infinity and directed towards the vapour plume 10. In order to aid direction of the spectrometer 12 towards the vapour plume 10, the infrared spectrometer 12 is situated on a platform 16 approximately 3m above the ground. The telescope lens 14 and the infrared spectrometer 12 together are able to record emission data from the vapour plume 10. These data are then processed by the processing unit 18 to produce a spectra. The processing unit 18 is then able to compare the spectra to a known library to positively identify the one or more components in the liquid sample.

Examples

The following examples further illustrate the preferred embodiments within the scope of the present invention. These examples are given solely for the purpose of illustration and are not to be construed as limitations of the present invention as many variations of the invention are possible without departing from its spirit or scope.

Example 1

A continuous wave CO_2 laser (Edinburgh Instruments), operating at 9.6 μm, with an output power of 4.5 W, was situated approximately 1 m away from a droplet of liquid methyl salicylate of approximate diameter 10 mm. The laser beam was directed using appropriate mirrors and focussed on to the droplet using a lens made of zinc selenide and then used to vaporise the sample to create a vapour plume directly above the

droplet. The infrared emission spectrum of the vapour plume was then measured using a MIDAC AM Fourier Transform Infrared (FTIR) spectrometer, with 1 m focal length collection lens placed in front of the open emission port, situated 1 m away from the vapour and positioned at right angles to the laser. The infrared spectrum was obtained by operating the FTIR at between 1 and 20 scans per second and using a suitable resolution of 1 to 32 cm^{-1}. The collected spectra were compared with library spectra to provide positive identification of the liquid methyl salicylate from its vapour. Successful analytical results have also been achieved by modifying the system to use a 2 m focal length lens or a 3 m focal length lens and moving the FTIR spectrometer to a distance of 2 m or 3 m from the plume respectively.

Example 2

A continuous wave CO_2 laser (Edinburgh Instruments), operating at 9.25 μm, with an output power of 10 W, was situated approximately 5 m away from a droplet of liquid chemical warfare agent of approximate diameter 10 mm. The laser beam was directed unfocussed on to the droplet and then used to vaporise the sample to create a vapour plume directly above the droplet. The infrared emission spectrum of the vapour plume was then measured using a MIDAC AM Fourier Transform Infrared (FTIR) spectrometer, fitted with a Cassegrain telescope with a diameter of 25 cm focused to infinity, situated 5 m away from the vapour and positioned alongside the laser. The infrared spectrum was obtained by operating the FTIR at between 1 and 20 scans per second and using a suitable resolution of 1 to 32 cm^{-1}. The collected spectra were compared with library spectra to provide positive identification of the individual components of the liquid chemical warfare agent mixture.

CLAIMS

1. A method, suitable for stand off analysis of a sample (2) comprising one or more chemical and/or biological warfare agents of low volatility, said method comprising:

(i) using an excitation means (6) to vaporise the sample thereby producing a vapour plume (10) of molecular species; and

(ii) using an analytical means (12, 18) to analyse the molecular species within the vapour plume (10) wherein the analytical means analyses the molecular emission spectra of the vapour plume and is provided with means (14) to enable it to receive said spectra for stand off analysis.

2. A method according to Claim 1 wherein the excitation means (6) is a laser.

3. A method according to Claim 2 wherein the laser is operated at a fixed wavelength.

4. A method according to Claim 2 or Claim 3 wherein the laser has a power of greater than 2 W, preferably greater than 5 W, and more preferably greater than 10 W.

5. A method according to any of Claims 2 to 4 wherein the laser has a power of less than 150 W, preferably less than 50 W, more preferably less than 20 W.

6. A method according to any of Claims 2 to 5 wherein the laser is operated as continuous laser beam.

7. A method according to any of Claims 2 to 6 wherein the laser is a carbon dioxide laser.

8. A method according to any of Claims 1 to 7 wherein the method comprises the use of only a single excitation means (6).

9. A method according to any of Claims 1 to 8 wherein the vapour plume (10) is hotter than the surrounding atmosphere by at least 0.1K.

10. A method according to Claim 9 wherein the vapour plume is hotter than the surrounding atmosphere by 1K.

11. A method according to Claim 10 wherein the vapour plume is hotter than the surrounding atmosphere by 5K.

12. A method according to any of Claims 9 to 11 wherein the analytical means (12, 18) is an infrared spectrometer, preferably a Fourier transform infrared spectrometer.

13. A kit suitable for stand off analysis of a sample comprising one or more chemical and/or biological warfare agents of low volatility, said kit comprising:

(i) an excitation means (6) arranged such that it can be used to vaporise the sample thereby producing a vapour plume (10) of molecular species;

(ii) an analytical means (12, 18) arranged to analyse the emission spectra of the molecular species within the vapour plume; and

(iii) means (14) associated with the analytical means (12, 18) to enable said analytical means to receive the emission spectra from the vapour plume.

14. An apparatus suitable for stand off analysis of a sample comprising one or more chemical and/or biological warfare agents of low volatility, said apparatus comprising:

(i) an excitation means (6) arranged such that it can be used to vaporise the sample thereby producing a vapour plume (10) of molecular species;

(ii) an analytical means (12, 18) arranged to analyse the emission spectra of the molecular species within the vapour plume; and

(iii) means (14) associated with the analytical means (12, 18) to enable said analytical means to receive the emission spectra from the vapour plume.